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(54) Multilayer printed wiring board and method for making same.

(57) A multilayer printed wiring board is disclosed having (a) an inner layer conductive pattern on an organic insulating base material; (b) a poly(vinyl acetal)-phenolic resin coating containing an amine substituted organic zirconate or titanate coupling agent; (c) a dielectric insulating layer; (d) a bonding composition capable of being adhesion promoted for electroless metal deposition comprising a phenolic resin having at least two methylol groups and substantially free of methyl ether groups, a heat resistant aromatic or cyclic resin having functional groups capable of reacting with the methylol groups without the evolution of water; and (e) an outer conductive pattern, the multilayer board being capable of withstanding at least five soldering cycles of at least 255°C for 2 seconds without blistering or delamination. Processes for the manufacture of the inventive multilayer boards are also disclosed.

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MULTILAYER PRINTED WIRING BOARD AND METHOD FOR MAKING SAME

This invention relates to multilayer printed wiring boards and method for making such boards. The invention is also related to printed wiring boards made by the additive technique.

Multilayer printed wiring boards are commonly manufactured by the subtractive technique. In the conventional subtractive process, the inner layers are prepared on thin, copper clad epoxy glass laminate, typically 0.1 to 0.2 mm thick, by etching away the unwanted copper. The inner layers are assembled in a stack with B-staged epoxy prepreg sheets between the layers and laminated together with sheets of copper foil on the outside surfaces of the stack. Holes are drilled through the multilayer laminate and the hole walls are plated to establish plated through hole connections to the internal layers. Then, the outer layers of copper foil are etched to provide the outer layer conductive patterns.

In the "mass molded" multilayer process, the operations of etching the custom conductive patterns for the inner layers and the lamination of the inner layers together with the outer layers of copper foils are carried out in central laminating plants. Then, the laminated package is sent to individual printed wiring board manufacturers who perform the operations of drilling, forming plated through holes and etching the outer surface conductor patterns to complete the multilayer board. When a completed "mass molded" board is examined by a purchaser or user, there is no obvious difference in appearance, form or function from the multilayer boards made by the standard multilayer process.

Additive multilayer boards have been made by the "mass molding" technique. The conductive patterns for the inner layers were etched in a subtractive process. The inner layers were laminated together as in the regular "mass molding" technique, but the outer surfaces were C-staged epoxy coated glass cloth, not copper. These "mass molded" packages were finished by additive printed wiring board manufacturers who applied first a plating adhesive to each surface, next drilled the through holes, and then applied a plating resist and plated the conductive pattern on the outer surfaces and through the holes to complete the multilayer board. This manufacturing procedure did not offer significant price or functional advantages over fully subtractive "mass molded" multilayer board manufacturing and has not been widely adopted. A multilayer board made by an additive process and the "mass molding" technique has a different appearance from multilayer boards made by the subtractive processes.

Other methods of making multilayer printed wiring boards start with a thicker inner layer laminate (0.2 mm to 1 mm thick) which is copper clad on both sides. The inner layer conductive patterns are etched. Instead of laminating all the layers together in a laminating press, the layers are built up sequentially on the thick inner layer laminate by adding in sequence, an insulating layer, and then another conductive pattern layer. The conductive pattern is added either by fully-additive, semi-additive or subtractive processes. In the fully-additive processes, the conductive pattern is plated directly. In the semi-additive and subtractive processes, a complete layer of copper is applied over the insulating layer and then the conductive pattern established by plating and etching. Multilayer boards made sequentially by either fully-additive processes or semi-additive processes have a distinct different appearance which is obvious to the purchaser or user.

Multilayer printed wiring boards are commonly provided with internal ground and power planes. These internal planes are frequently solid sheets of copper only interrupted by clearance holes (the perforations required for electrically isolating the through hole pattern of the printed wiring board). These ground and power planes provide power voltage and current and ground connections for the components of the multilayer printed circuit. A second function of the ground and power planes is to provide electromagnetic shielding for the multilayer printed circuit board and reduce the electromagnetic and radio frequency interference. Multiple ground and power planes and additional ground planes or shields on the surface layers with the conductive pattern are common.

When components are mounted on a multilayer printed wiring board and mass soldered in place at temperatures in the range of 275°C, a severe thermal shock is applied to the insulating layers placed between two copper planes, such as the insulating layer between an internal ground plane and ground shield on the surface surrounding the conductor pattern. Frequently, delamination will occur and blisters will form between the ground shield on the surface and the internal ground or power plane. Delamination and blistering has been a problem with multilayers made by the fully-additive, semi-additive or subtractive sequential processes.

In the multilayer printed wiring board, an application of strongly adherent oxide layers on copper has been adopted to enhance the bond between the copper conductive patterns and the insulating layers. The oxide layers are used in the press laminating processes as well as the sequential processes. Such strongly adherent oxide layers

are usually applied by immersing the copper surface in hot (40° -110°C), strongly alkaline, hypochlorite solutions. This immersion produces an adherent, black, dendritic, oxide layer with a high surface area for adhering to organic films, coatings and laminated layers. In the printed wiring industry, this oxide layer is commonly called "black oxide".

The black oxide layer is subject to attack by solutions which dissolve copper oxides. Use of such solutions are necessary in multilayer board manufacturing. In multilayer board manufacturing, the inner copper planes are coated with black oxide, and the outer layers of insulator and copper laminated over them. When holes are drilled through the multilayer laminate and the hole walls are plated to create electrical connections to the inner copper planes, the plating and cleaning solutions dissolve the black oxide surrounding the holes and leave a non-adherent ring around the hole. This is known in the industry as "pink ring" because a pink ring of copper is visible in the pattern of black oxide coated copper. At the pink ring, there is no adhesion between the copper plane and the laminated insulating layer over it. Ionic contamination and failure of insulation between holes occur where pink rings are found. Pink rings have been a severe problem for additively and sequentially manufactured multilayer boards. In accordance with the invention, there is provided an additive multilayer printed wiring board comprising

(a) an inner layer of an organic insulating base material having a copper conductive pattern adhered thereto;

(b) a thermoset primer coating covering at least a portion of the conductive pattern and the insulating base material, said thermoset primer coating composition being comprised of the product of reaction between 20 to 60% by weight of a poly(vinyl acetal) resin with 80 to 40% by weight phenolic resin in the presence of an acidic catalyst and a coupling agent having at least two amino-substituted aromatic groups covalently bonded to a titanium or zirconium central atom via an oxygen containing linkage, said coupling agent coupling to the metal surface and firmly bonded to the phenolic resin and being present in the primer coating composition in an amount sufficient to couple the poly(vinyl acetal) phenolic resin reaction product to the metal surface;

(c) a layer of an organic dielectric insulating material covering at least part of the thermoset primer coating;

(d) a layer of a thermoset bonding composition covering at least part of the layer (b) and cured thereon, said bonding composition being comprised of a phenolic resin substantially free of methyl ether groups and having an average of between 4 and 10 phenolic rings per molecule and at least two methylol functional groups, at least one heat resistant polymer having an aromatic or cyclic backbone and functional groups capable of crosslinking with phenolic methylol groups without evolving water, said heat resistant po lymer(s) being present in an amount sufficient to react with substantially all the methylol groups of the phenolic resin, said polymer with aromatic or cyclic backbones being capable of improving the electrical or heat resistant properties of said bonding composition, and an elastomer selected from the group consisting of neoprene, nitrile rubber and chlorosulfonated polyethylene, and vinyl and acrylic elastomers, said elastomer being 30 to 60% of the combined weight of the phenolic and heat resistant resins and elastomer.

The primer coating composition further comprises a mineral filler in an amount of at least 20 parts and less than 60 parts filler per 100 parts of the poly(vinyl acetal) phenolic resin reaction product, and preferably at least 30 parts and less than 50 parts, sufficient to substantially eliminate smear of the primer coating composition in walls of holes when holes are drilled through the primer coating, and less than an amount that will cause torsion fracture of the interface between the primer coating and the metal surface. The filler is selected from the group consisting of wollastonites and attapulgites and combinations thereof. The primer coating composition still further comprises a coupling agent in an amount between 0.3 and 2% by weight of the total resin content of the primer coating composition and sufficient to wet out and couple the filler to the poly(vinyl acetal) phenolic resin reaction product. The coupling agent may be selected from the group consisting of neoalkoxy tris(3-amino)phenyl zirconates and titanates.

The polymer with aromatic or cyclic backbones is selected from the group consisting of cyclic aliphatic epoxy resins and bisphenol A epoxy resins having an average of between 1.5 and 3 epoxide functional groups per molecule and an epoxy equivalent weight between 170 and 2500, and bismaleimide-triazine polymer resins.

There is also provided a process for manufacturing a multilayer printed wiring board comprising the steps of

- establishing at least one inner layer conductive pattern on an organic insulating base material;
- coating at least a portion of the inner layer conductive pattern and the insulating base material with the primer coating composition of claim 1 which, when cured, firmly bonds to the conductive pattern and the base material, and which comprises a sufficient amount of organic solvent to dissolve the resins and coupling agent and establish a viscosity for the coating composition suitable for applying it to a substrate;

- curing said primer coating composition and applying an organic dielectric insulating layer thereon which is also cured thereby firmly bonding it to said primer coating;
- applying the bonding composition of claim 1 for adherently plating metal thereon;
- curing said bonding composition; and
- electrolessly plating a metallic conductive pattern securely adhered to said bonding composition thus creating a multilayer printed wiring board having adhesion between said layers capable of withstanding exposure to at least 5 cycles of soldering of at least 255°C for 2 seconds without blistering or delamination between the layers.

The primer coating composition is applied on the carefully cleaned surface(s) of the insulating base material. The clean surface is provided by an abrading process carried out with an abrasive in the presence of water.

The curing of the primer coating composition is carried out at a first temperature sufficient to drive off the solvents and initiate a curing reaction and at a second temperature higher than the first to complete the curing reaction.

The multilayer printed wiring boards of the invention are capable to withstand exposure to at least 5 soldering cycles of at least 255°C for 2 seconds per cycle without blistering or delamination between the layers. They are also capable of maintaining the bond of the deposited metal for at least 10 seconds at a temperature of 430°C.

Figs. 1A to 1H are cross section views in sequence of a multilayer board as manufactured by the process of the invention.

The multilayer printed wiring board according to the invention is constructed on an organic insulating base material having a copper conductive pattern thereon. The base material may be selected from those suitable for the printed wiring board industry such as phenolic-paper laminates, epoxy-paper laminates, epoxy-glass laminates, epoxy-glass composite laminates, polyimide and triazine resin laminates and other base materials having adequate thermal and electrical properties. A preferred organic insulating base material is a glass reinforced thermosetting resin laminate such as epoxy-glass. In one embodiment of the invention, the base material is catalytic for electroless metal deposition as described in US Patent 3,546,009.

According to the invention, the conductive pattern on the base material may be provided by a subtractive process of etching a copper clad laminate.

In one embodiment, the conductive pattern is provided by an additive process on an adhesive coated laminate as shown in Fig. 1A, the laminate being designated 10 and the adhesive coating 11.

In Fig. 1B, a permanent plating resist, 12, is printed over the adhesive surface. Suitable permanent plating resists are well known to those skilled in the art of additive processes. After the resist image is exposed and developed, or in the case of a screen resist, UV-cured, the image is oven baked for 30 min. at 160° to ensure complete cure and that no volatiles remain.

In Fig. 1C, a copper conductive pattern, 13, is plated by an additive process on the base material. Preferably, the thickness of the copper conductive pattern and the permanent plating resist are substantially equal so the next layer can be applied to a level surface.

Nonpermanent resists which are stripped after the conductive pattern is plated may also be used, but do not provide a level surface for applying the layer over the conductive pattern. The conductive patterns produced by subtractive process also do not provide a level surface for the application of the next layer. In these cases, the surface can be leveled by applying a filling material between the edges of the conductive pattern, or the subsequent layers may be applied thicker to ensure adequate coverage and insulation between layers.

The electrolessly plated copper layer is usually 35-40 micrometers thick and the permanent resist layer is 25-40 micrometers thick. After plating the base material, now provided with a copper conductive pattern, is cleaned, rinsed, dried and post cured at 160°C for 1 hour.

After the post cure, one side of the base material with its conductive pattern is scrubbed with pumice, rinsed, blown dry with an air knife and oven dried for only 1 minute at 150°C. The oven drying is kept short to avoid heavy oxidation of the plated copper surface.

In Fig. 1D, a primer layer, 14, is applied over at least a portion of the plated copper conductive pattern and the Insulating base material either by reverse roller coating, curtain coating or blank screen printing. The primer layer is applied to achieve a film thickness when dried of at least 20 micrometers, preferably 25 to 35 micrometers. The primer is a poly(vinyl acetal)-phenolic resin composition which firmly bonds to the copper conductive pattern and the base material, said resin composition containing an amount of amino terminated coupling agents selected from the group consisting of amino terminated organic zirconates and titanates, said coupling agent being present in an amount sufficient to contribute heat and chemical resistance to the bond between the copper surface and the poly(vinyl acetal)-phenolic coating. Suitable primers are described in co-pending application No. filed on even date. One such suitable primer has the composition given below:

A solution containing: 100 g

poly(vinyl butyral) 25 %
resole phenolic resin 50 %
butyl acetate 25 %
Wollastonite (particle size less than 10 μm having 1 m^2 surface area per g) 55 g
Neoalkoxy tris(3-amino)phenyl zirconate 1.6 g
Defoamer 1.0 g
Butyl acetate 5.0 g
2-(2-butoxyethoxy)ethanol 5.0 g
Clay filler containing 1200 ppm Pd 2.0 g

This produced a viscosity of 30 to 40 Pa suitable for serigraphy, and the coating is applied serigraphically, and dried and partially cured at 120°C for 20 minutes. Othersuitable primers have the composition of the primer described above except that a phenolic resin-poly(vinyl butyral) blend is substituted for the above, and contain either a neoalkoxy tris(3-amino)phenyl titanate or the neoalkoxy tris(3-amino)phenyl zirconate. The phenolic resin-poly(vinyl butyral) blend contains 40% phenolic resole resin, 50% polyvinyl butyral and 10% solvent. The procedure for scrubbing, drying and applying a primer layer is repeated for the conductive pattern and organic insulating base material on the second side of the base material.

An insulating dielectric layer. 15 in Fig. 1D, is applied, e.g., by either blank screen or reverse roller coating. The thickness of the coating may be varied to obtain the required impedence for the conductive pattern. A coating thickness of at least 80 micrometers is preferred.

Epoxy solder masks are suitable as the insulating dielectric layer. These masks are well known in the art. When used in this manner as the insulating layer for multilayer boards made by sequential additive processes, the solder masks are modified by the addition of a catalyst for electrolessly plating metal. Among the solder masks that may be used is a curing agent modified by the addition of 4 g of the clay filler containing 1200 ppm Pd per 100 g. Another solder mask is modified with 40 g wollastonite, 2 g neoalkoxy tris(3-amino)phenyl titanate, 4 g clay filler containing 1200 ppm Pd and 5 g 2-(3-butoxyethoxy) ethanol per 100 g of solder mask. To improve the resistance to thermal stress shorten the chemical desmearing process after drilling, the solder mask can be further modified by the addition of 25 g of an epoxy novolac flexibilizer and an additional 30 g wollastonite.

The liquid dielectric coating is applied to one side of the primer coated panel. For the thermally cured dielectric coatings above, the coated panel is heated to 120°C for 20 minutes to level the coating and remove solvents. This procedure is repeated until the required thickness, of the dielectric layer is obtained. The thickness is preferably at least 70 micrometers. With a properly adjusted screen printing machine, this can be achieved in 2 coats. With a roller coater, it can be achieved in one coat. At least two coats are preferred to ensure no pinholes in the dielectric coating. The thickness of the dielectric layer can be changed as required in order to obtain a controlled impedence conductive pattern.

The coating procedure is repeated to apply an insulating dielectric coating to the second side of the board. Then the board is baked for 20 minutes at 160°C to partially cure the dielectric coating and remove all volatile solvents.

An insulating dielectric layer cured by ultraviolet radiation also may be used. A suitable ultraviolet curable composition:

UV DIELECTRIC 3.4-epoxycyclohexylmethyl-3.4-epoxycyclohexane carboxylate 52 g
Epoxy based flexibilizing agent for cycloaliphatic epoxide coating systems 48 g
Triaryl sulfonium salt photoinitiator $(C_6H_5)_3S\ SbF_6$ 0.75 g
Clay filler containing 1200 ppm Pd 10 g
Defoamer 2 g
Fluoroaliphatic polymeric ester for levelling and flow control 0.1 g
Fumed silica 5 g

The UV cured coatings are cured with about 2 joules/cm^2 of ultraviolet radiation. The second side is coated in the same way.

The surface of the dielectric coating is examined for protrusions which may interfere with the next layer. The protrusions were smoothed and leveled on the both surfaces with abrasive paper, and then scrubbed with pumice, rinsed and dried.

A bonding composition, 16 in Fig. 1E is applied over the insulating dielectric layer. The bonding composition may be applied in solution as a liquid by serigraphic, reverse roller or curtain coating techniques, or it may be applied as an uncured dry film by press, vacuum or hot roll lamination.

The bonding composition comprises polymeric materials or blends of polymeric materials which are capable of being cured, being adhesion promoted after curing and being adherently plated with metal. The bonding composition after post cure does not liquify or evolve volatiles below 288°C. Suitable bonding compositions are described in co-pending application No. filed on even date. One such suitable bonding composition is formulated as follows:

Nitrile rubber 16.88 g
Chlorosulfonated polyethylene rubber 5.67 g
Palladium catalyst (1%) dispersed in a liquid epoxy resin with an epoxide equivalent weight of 180 3.32 g

Zirconium silicate filler 11.45 g
Fumed silica 0.27 g
High flash aromatic naphta, with 82-88% aromatics and a boiling range of 150-200°C 11.48 g
2-ethoxyethyl acetate 28.76 g
2-methylphenol-formaldehyde resin with an average degree of polymerization of 8 6.97 g
Solid diepoxide bisphenol A resin with an epoxide equivalent weight of 500 12.03 g
Flow promoter 0.97 g
Catalytic clay filler cont. 1200 ppm Pd 1.93 g
Neoalkoxy tris(3-amino)phenyl zirconate 1.40 g

Another suitable bonding composition is formulated as follows:

Phenolic resin 11.0 g
Polyvinyl butyral resin 15.0 g
Diepoxide bisphenol A resin (epoxide equiv. weight 850-975) 22.0 g
Catalytic filler (cont. 1200 ppm Pd) 4.0 g
Neoalkoxy tris(3-amino)phenyl zirconate 1.4 g
Flow promoter 1.0 g
Defoamer 1.0 g
Zirconium silicate filler 15.0 g
2-(2-butoxyethoxy)ethanol 20.0 g
Trifunctional phenolic resin (average of 8 phenol groups per molecule) 11.2 g
Nitrile rubber 22.4 g
Bismaleimide-triazine resin 22.4 g

Another suitable bonding composition is formulated as follows:

Trifunctional phenolic resin (average of 8 phenol groups per molecule) 11.2 g
Nitrile rubber 22.4 g
Bismaleimide-triazine resin 22.4 g

Another suitable bonding composition is formulated as follows:

Phenolic resin 14.5 g
Polyvinyl butyral resin 14.5 g
Bismaleimide-triazine resin 29.0 g
Butyl acetate 30.0 g
Neoalkoxy tris(3-amino)phenyl zirconate 1.4 g
Flow promoter 1.0 g
Defoamer 1.0 g
Zirconium silicate filler 12.0 g
Zinc octanoate 0.015 g

Another suitable bonding composition is formulated as follows:

Phenolic resin 8.8 g
Polyvinyl butyral resin 11.8 g
Bismaleimide-triazine resin 29.4 g
2-(2-butoxyethoxy)ethanol 30.0 g
Neoalkoxy tris(3-amino)phenyl zirconate 1.4 g
Zirconium silicate filler 12.0 g
Catalytic clay filler w. 1200 ppm Pd 4.0 g
Defoamer 1.0 g
Flow promoter 1.0 g
Zinc octanoate 0.015 g

The viscosity of the bonding composition solution is adjusted to 0.5 Pa•s with 2-ethoxyethyl acetate. The dielectric coated board is brushed, rinsed, hot air dried and the bonding composition is applied by the curtain coating technique. The bonding composition is dried in a tunnel drier, and the second side of the board is coated by the same procedure. Then the bonding composition was cured for 1 hour at 160°C. The film thickness of the bonding composition layer is 25-30 micrometers thick after drying and curing. This heating step also finally cures the primer resin and the dielectric resin layers.

Through holes, 17 in Fig. 1F are drilled through the panels. The holes contact the internal conductive pattern, 13, where required. Through holes that are required not to contact the internal conductive pattern are drilled through the permanent resist pattern, 12.

After drilling the board is scrubbed with pumice, rinsed and washed with high pressure water spray to remove drilling debris.

A permanent resist pattern, 18, outlining the surface conductive pattern of the outer layer is printed on both sides of the board, and then the panel is heated for 30 minutes at 120°C to insure complete cure of the resist and removal of developing solvents.

The portion of the bonding composition not covered with the resist is adhesion promoted and the walls of the drilled holes desmeared simultaneously by immersion for 8 minutes at 52°C in a chromic acid adhesion promotion solution containing chromic acid - 40 g/l, sodium fluoride - 20 g/l and sulfuric acid - 12 N. This is followed by a dragout rinse, a two step neutralization in sodium sulfite solution and a two stage counter current rinse

Copper is electrolessly plated on the surface conductive Patterns, 19, and through the holes, 20, establishing a complete additively produced sequential multilayer board.

After plating copper the board is brushed in a brushing machine, rinsed, dried and post cured at 120°C for 1 hour followed by 160°C for 1 hour.

For test purposes a multilayer board had been provided with a copper surface conductive pattern containing a 75mm x 75mm ground shield above a solid inner conductive pattern ground shield of the same dimensions. This ground shield was a solid copper pattern fre~ from the perforations and cross hatching required in prior art ground shields of this size to prevent blistering or delamination under thermal shock. A multilayer board manufactured by the process of this invention above was thermally shocked by five cycle through a hot air solder levelling machine. Each cycle consisted of cleaning, fluxing, preheating, 2 second immersion in molten solder at 255°C, blowing off excess solder

with hot air, cooling and a water wash. After five cycles the multilayer was examined for blisters or delamination in areas where a surface ground shield is over an inner layer ground shield. there was no blistering or delamination even in the unbroken ground shield areas.

The processes of this invention economically produce an additive, sequential multilayer board with thermal properties equal or superior to conventional subtractive multilayer boards or prior art additive multilayer boards. It allows the circuit designer to take advantage of the higher density designs available in additive processes compared to subtractive and at the same time the designer does not have to sacrifice the thermal resistance previously only available in the subtractive laminated multilayer.

Claims

1. An additive multilayer printed wiring board characterized in that it comprises

(a) an inner layer of an organic insulating base material having a copper conductive pattern adhered thereto;

(b) a thermoset primer coating covering at least a portion of the conductive pattern and the insulating base material, said thermoset primer coating composition being comprised of the product of reaction between 20 to 60% by weight of a poly(vinyl acetal) resin with 80 to 40% by weight phenolic resin in the presence of an acidic catalyst, and a coupling agent having at least two amino-substituted aromatic groups covalently bonded to a titanium or zirconium central atom via an oxygen containing linkage, said coupling agent coupling to the metal surface and firmly bonded to the phenolic resin and being present in the primer coating composition in an amount sufficient to couple the poly(vinyl acetal) phenolic resin reaction product to the metal surface;

(c) a layer of an organic dielectric insulating material covering at least part of the thermoset primer coating;

(d) a layer of a thermoset bonding composition covering at least part of the layer (b) and cured thereon, said bonding composition being comprised of a phenolic resin substantially free of methyl ether groups and having an average of between 4 and 10 phenolic rings per molecule and at least two methylol functional groups, at least one heat resistant polymer having an aromatic or cyclic backbone and functional groups capable of crosslinking with phenolic methylol groups without evolving water, said heat resistant polymer(s) being present in an amount sufficient to react with substantially all the methlyol groups of the phenolic resin, said polymer with aromatic or cyclic backbones being capable of improving the electrical or heat resistant properties of said bonding composition, and an elastomer selected from the group consisting of neoprene, nitrile rubber and chlorosulfonated polyethylene, and vinyl and acrylic elastomers, said elastomer being 30 to 60% of the combined weight of the phenolic and heat resistant resins and elastomer.

2. The printed wiring board of claim 1, characterized in that the primer coating composition further comprises a mineral filler in an amount sufficient to substantially eliminate smear of the primer coating composition on walls of holes when holes are drilled through the primer coating, and less than an amount that will cause torsion fracture of the interface between the primer coating and the metal surface, and that a coupling agent is also present in an amount sufficient to wet out and couple the filler to the poly(vinyl acetal) phenolic resin reaction product.

3. The printed wiring board of claims 1 or 2, characterized in that the amount of coupling agent is between 0.3 and 2% by weight of the total resin content of the primer coating.

4. The printed wiring board of claim 2, characterized in that the filler is present in an amount of at least 20 parts and less than 60 parts filler per 100 parts of the poly(vinyl acetal) phenolic resin reaction product.

5. The printed wiring board of claim 4, characterized in tha the filler is present in an amount of at least 30 parts and less than 50 parts filler per 100 parts of the poly(vinyl acetal) phenolic resin reaction product.

6. The printed wiring board of claims 1 to 5, characterized in that the filler is selected from the group consisting of wollastonites and attapulgites and combinations thereof, and the coupling agent is selected from the group consisting of neoalkoxy tris(3-amino) phenyl zirconates and titanates.

7. The printed wiring board of one or more of claims 1 to 6, characterized in that the polymer with aromatic or cyclic backbones is selected from the group consisting of cyclic aliphatic epoxy resins and bisphenol A epoxy resins having an avergae of between 1.5 and 3 epoxide functional groups per molecule and an epoxy equivalent weight between 170 and 2500, and bismaleimide-triazine polymer resins.

8. The printed wiring board of one or more of claims 1 to 7, characterized in that the bonding composition (d) further comprises fillers and coupling agents, and that said coupling agents are selected from the group consisting of amino substituted organic zirconates and titanates

9. A process for manufacturing a multilayer printed wiring board of one or more of claims 1 to 8, characterized in that the process comprises the steps of

- establishing at least one inner layer conductive pattern on organic insulating base material;
- coating at least a portion of the inner layer conductive pattern and the insulating base material with the primer coating composition of claim 1 which, when cured, firmly bonds to the conductive pattern and the base material, and which comprises a sufficient amount of organic solvent to dissolve the resins and coupling agent and establish a viscosity for the coating composition suitable for applying it to a substrate;
- curing said primer coating composition and applying an organic dielectric insulating layer thereon which is also cured thereby firmly bonding it to said primer coating;
- applying the bonding composition of claim 1 for adherently plating metal thereon;
- curing said bonding composition; and
- electrolessly plating a metallic conductive pattern securely adhered to said bonding composition thus creating a multilayer printed wiring board having adhesion between said layers capable of withstanding exposure to at least 5 cycles of soldering of at least 255°C for 2 seconds without blistering or delamination between the layers.

10. The process of claim 9, characterized in that the primer coating composition is applied on the carefully cleaned surface(s) of the insulating base material.

11. The process of claim 10, characterized in that the substantially clean surface(s) is (are) provided by an abrading process carried out with an abrasive in the presence of water.

12. The process of claim 9, characterized in that the curing of the primer coating composition is carried out at a first temperature sufficient to drive off the solvents and initiate a curing reaction and, subsequently, at a second temperature higher than the first to complete the curing reaction.

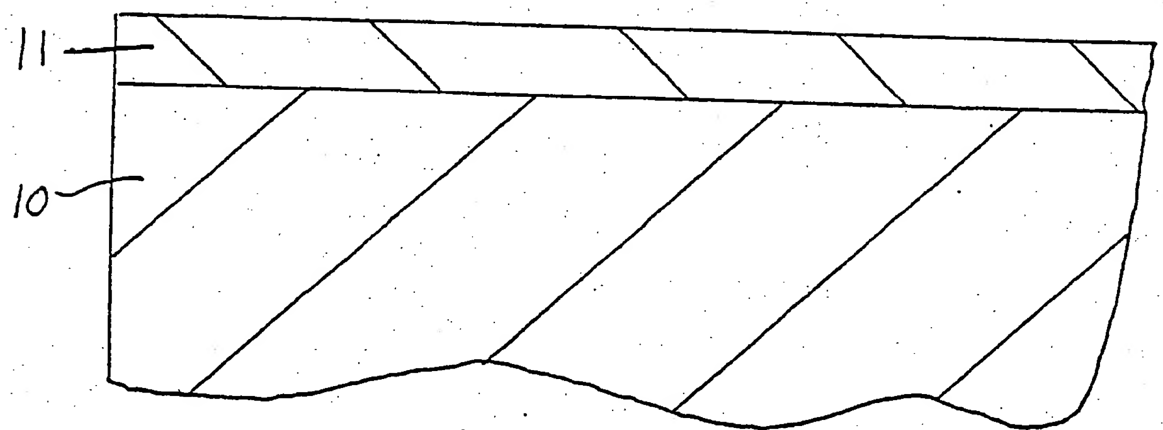

FIG. 1A

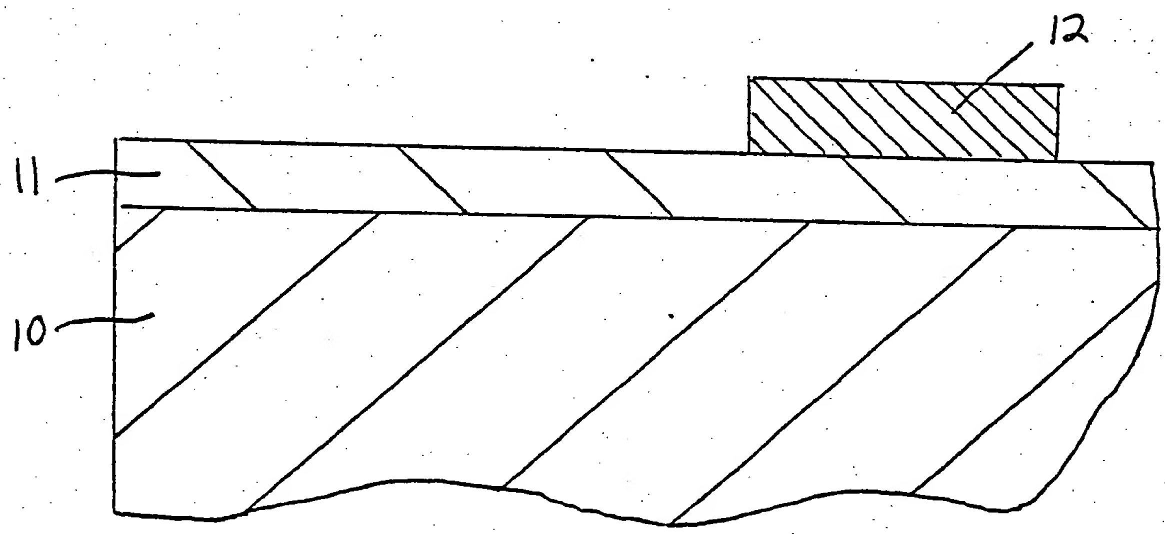

FIG. 1B

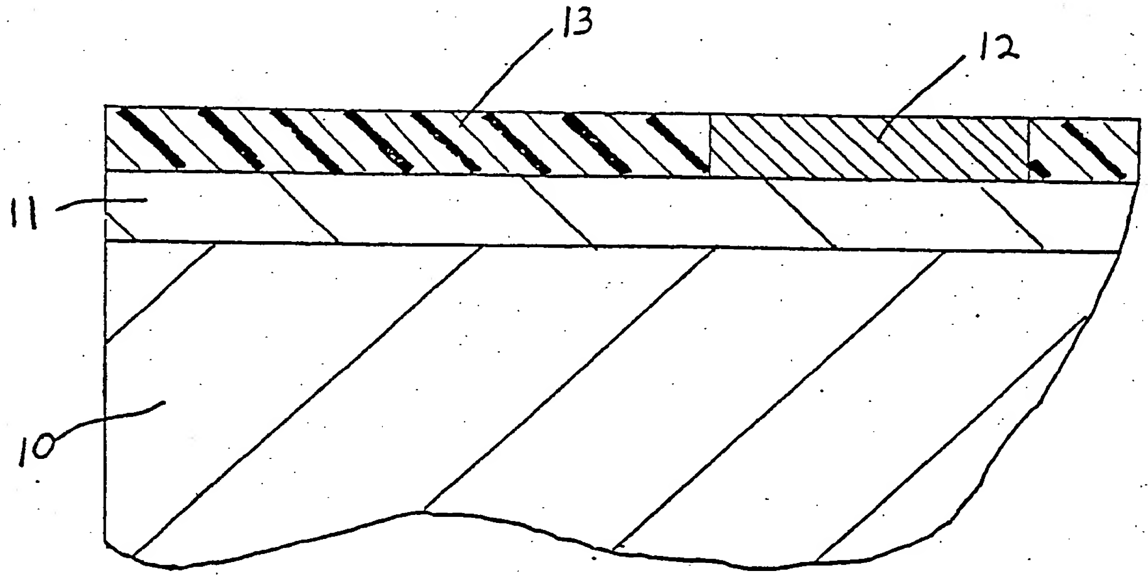

FIG. 1C

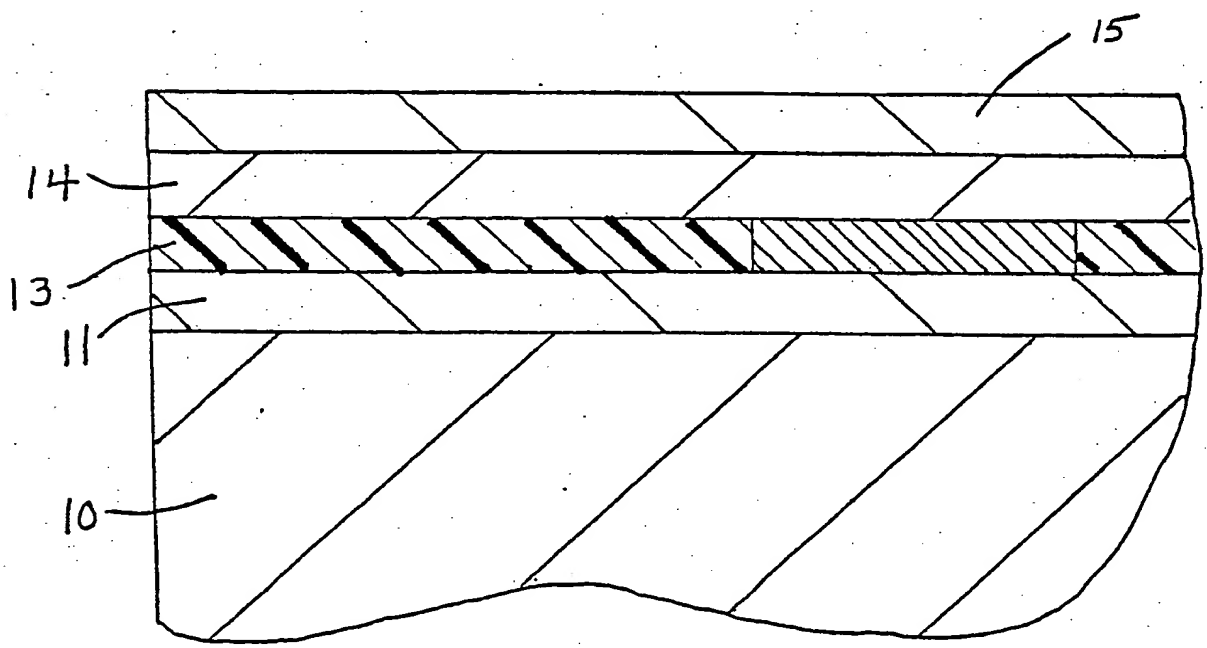

FIG. 1D

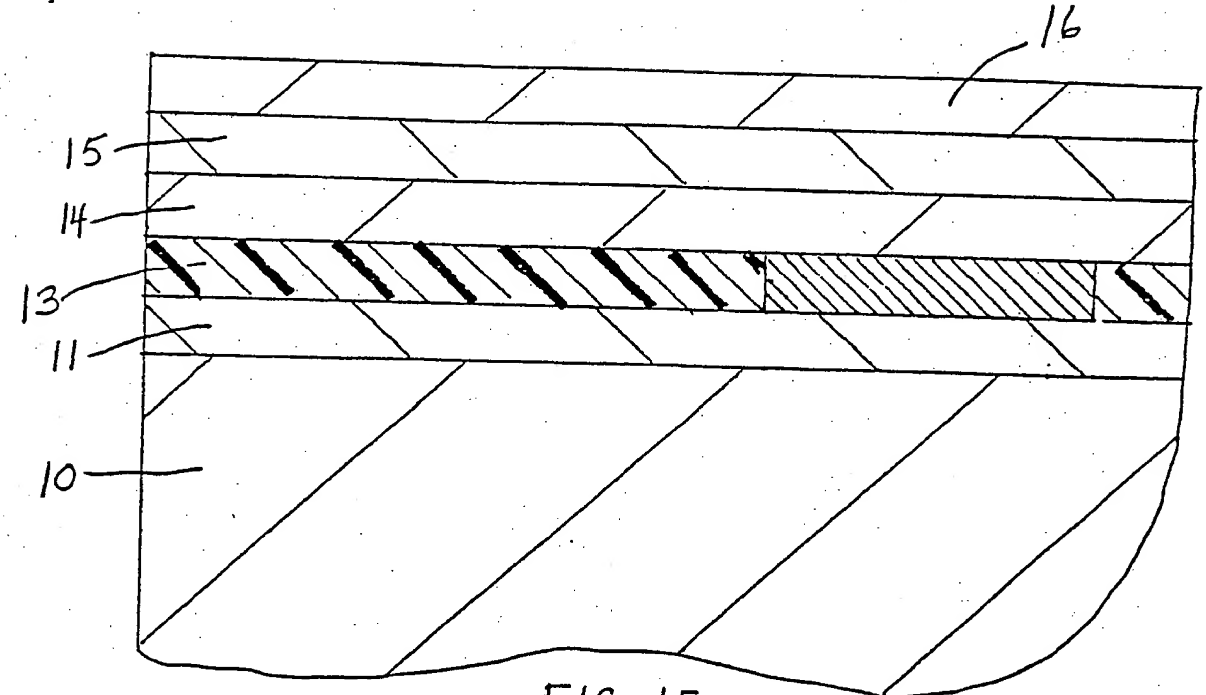

FIG. 1E

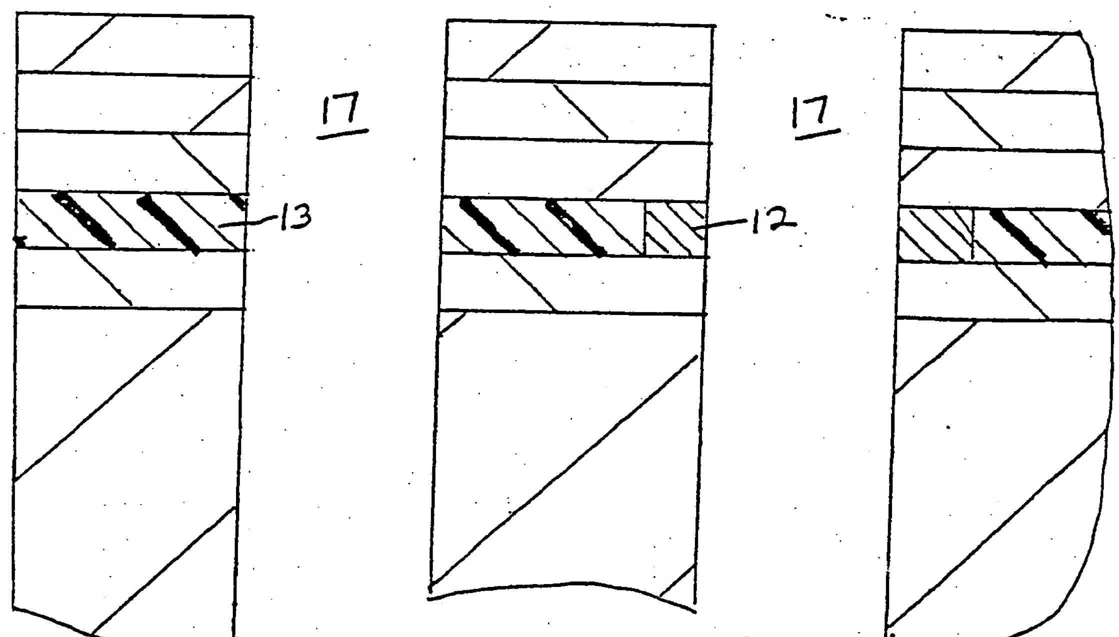

FIG. 1F

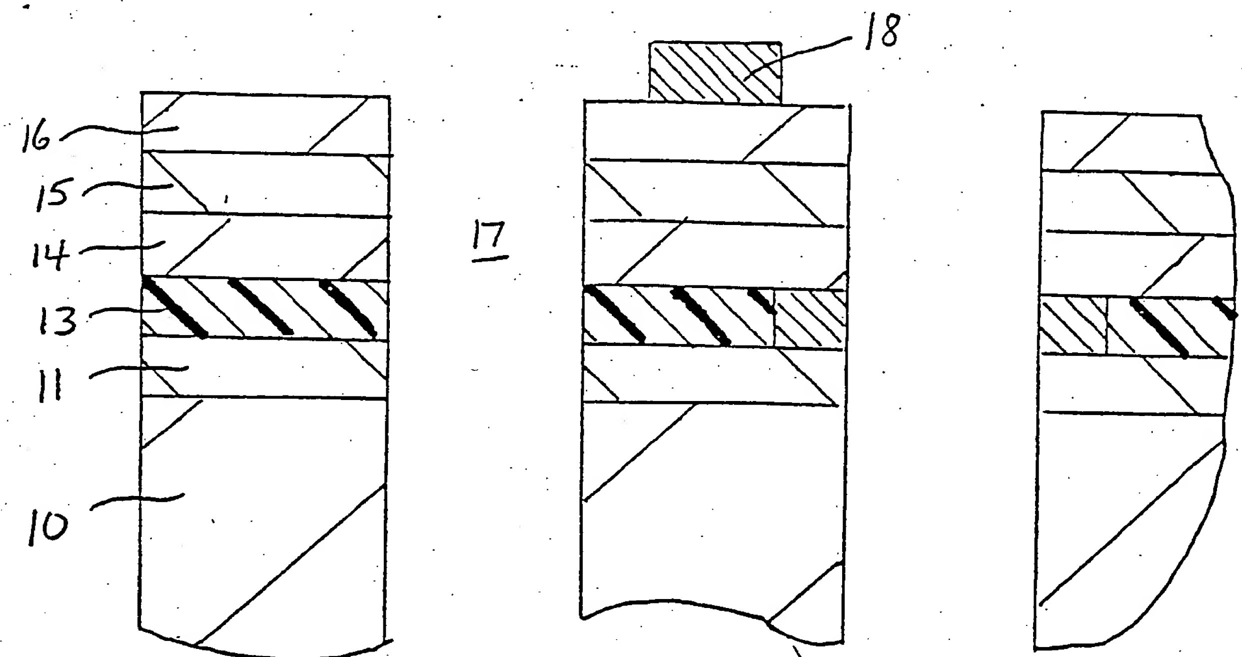

FIG. 1G

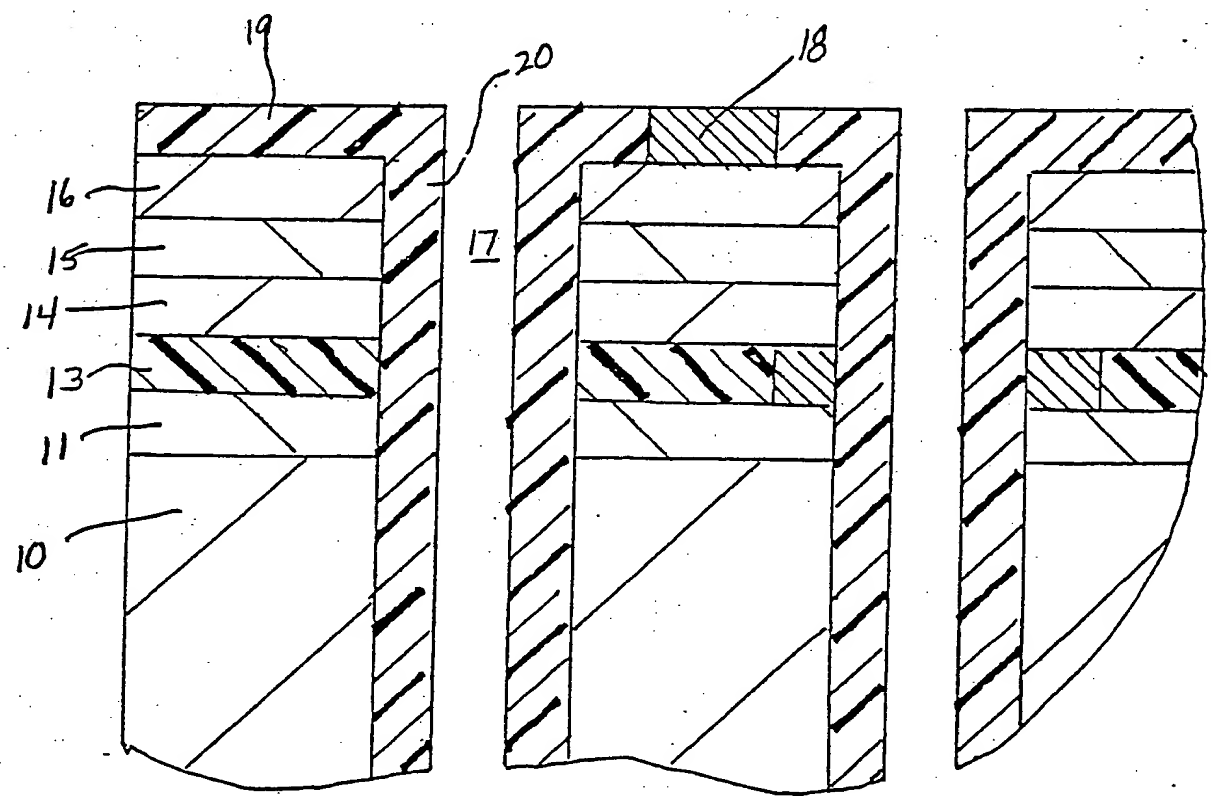

FIG 1H

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(54) **Multilayer printed wiring board and method for making same.**

(57) A multilayer printed wiring board is disclosed having (a) an inner layer conductive pattern (13) on an organic insulating base material; (b) a poly(vinyl acetal)-phenolic resin coating (14) containing an amine substituted organic zirconate or titanate coupling agent; (c) a dielectric insulating layer (15); (d) a bonding composition (16) capable of being adhesion promoted for electroless metal deposition comprising a phenolic resin having at least two methylol groups and substantially free of methyl ether groups, a heat resistant aromatic or cyclic resin having functional groups capable of reacting with the methylol groups without the evolution of water; and (e) an outer conductive pattern (19), the multilayer board being capable of withstanding at least five soldering cycles of at least 255°C for 2 seconds without blistering or delamination. Processes for the manufacture of the inventive multilayer boards are also disclosed.

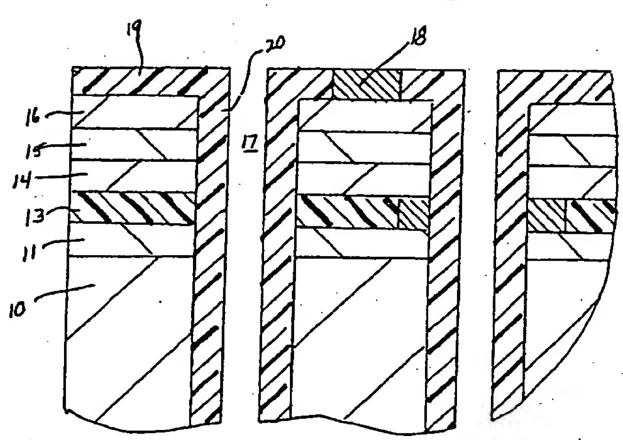

FIG 1H

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EUROPEAN SEARCH REPORT

Application Number

EP 88 10 0272

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	FR-A-2 476 427 (KOLLMORGEN CORP.) * Page 3, line 1 - page 5, line 19; page 6, lines 6-12; page 7, lines 10-13 *	1,9	H 05 K 3/46 H 05 K 3/38 C 09 J 3/00
A	DE-A-2 821 303 (HITACHI CHEMICAL CO.) * Page 12 - page 13, paragraph 1; page 26, last paragraph; page 28, paragraph 4 - page 29, paragraph 1 *	1,7-9	
A	US-A-3 471 589 (RINEHART) * Column 9, lines 14-30; column 10, lines 9-13; claim 5 *	1	
A	EP-A-0 164 227 (KENRICH PETROCHEMICALS) * Page 1, last paragraph - page 3, last paragraph; page 6, paragraph 4 - page 8 *	1-3,6,8	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			H 05 K C 23 C C 09 J C 09 D C 08 K

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	01-06-1989	MES L.A.

CATEGORY OF CITED DOCUMENTS

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